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(54) Components and catalysts for the polymerization of olefins

Bestandteil und Katalysator für Olefinpolymerisation

Composant et catalyseur pour la polymérisation d'oléfines

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Description

[0001] The present invention concerns catalysts for the polymerization of olefins and their use, particularly in the polymerization of $\text{CH}_2=\text{CHR}$ olefins, where R is a $\text{C}_1\text{-C}_6$ alkyl radical, an aryl radical, preferably phenyl, or a hydrogen atom.

[0002] Catalysts comprising titanium compounds supported on magnesium halides in active form are well known in the art. Catalysts of this type are described, for example, in US 4,278,718.

[0003] Said catalysts, although possessing high activity both in the polymerization of ethylene and alpha-olefins such as propylene, do not have adequate stereospecificity.

[0004] Said stereospecificity is improved by adding an electron-donor compound to the solid component comprising the titanium compound (US 4,544,713).

[0005] Further improvements have been obtained using both an electron-donor compound added to the solid component (internal donor) and one added to the Al-alkyl compound (external donor; US 4,107,414).

[0006] High performance, both in terms of activity and stereospecificity, is given by the catalysts described in European patent N. 0045977. The solid component of said catalysts comprises a magnesium halide in active form on which is supported a titanium halide (TiCl_4) and an electron-donor compound selected from specific classes of carboxylic acid esters, representative examples of which are the phthalates. The cocatalyst used is an Al-alkyl compound to which is added a silicon compound containing at least one Si-OR bond (R= hydrocarbyl radical).

[0007] US 4,522,930 describes catalysts where the solid catalyst component is characterized in that it contains an electron-donor compound, at least 70% in moles of which can be extracted with Al-triethyl under standard extraction conditions, and it has, after extraction, a surface area of at least $20 \text{ m}^2/\text{g}$.

[0008] Said catalysts comprise, as cocatalyst, an Al-trialkyl compound to which is added an electron-donor compound which does not undergo complexing reactions with Al-triethyl detectable by means of potentiometric titration under specified reaction conditions. Examples of the above mentioned electron-donor compounds are silicon compounds having Si-OR bonds where R is a hydrocarbyl radical; 2,2,6,6-tetramethylpiperidine, 2,2,5,5-tetramethylpyrrolidine, Al-diethyl-2,2,6,6-tetramethylpiperidide and Al-dichloromonophenoxy, Published European patent applications 0361494 and 0362705, describe ethers (having particular reaction and structural characteristics) used in the preparation of catalysts and catalyst components for the polymerization of the above mentioned olefins.

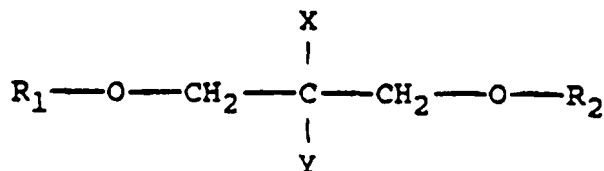
[0009] US-A-4,397,763 describes catalysts composed of a solid component comprising a titanium compound supported on magnesium chloride, a mixture of dihydrocarbyl aluminum compounds and an electron-donor compound selected from ether-alcohol compounds, specifically monoalkyl ethers of ethylene glycol or diethylene glycol.

[0010] However, the examples of said document show that the stereospecificity of these catalysts is low.

[0011] Now unexpectedly a new class of ethers has been found which is suited for the preparation of highly active and stereospecific catalysts for the polymerization of these olefins.

[0012] In fact, the ethers of the invention, together with Al-alkyl compounds and in combination with solid catalyst components having the characteristics described in US 4,522,930, form highly active and stereospecific catalysts.

[0013] The ethers of the invention contain two ether groups, and at least one heteroatom selected from the group consisting of N, S, P, Si, non-ether O and halogen atoms, or at least one double bond, or contain both at least one heteroatom as defined above and at least a double bond, and are selected from the group of 1,3-diethers of the formula



where

R_1 and R_2 are the same or different and are hydrocarbon radicals with 1-6 carbon atoms, optionally unsaturated and/or containing halogen atoms;

X is a hydrocarbon radical having 1-18 carbon atoms, containing at least one heteroatom which is not directly bonded to the central carbon atom (in the 2 position) of the 1,3-diether molecules, wherein the heteroatom is selected from the group consisting of N, S, P, Si, non-ether O and halogen atoms, or

X is a halogen atom or a heteroatom-containing group wherein one heteroatom is bonded directly to the central carbon atom of the 1,3-diether of the above formula and which is selected from the group consisting of $-\text{NR}'\text{R}''$, $-\text{SO}_2\text{R}'$, $-\text{SOR}'$, $-\text{OP}(\text{OR}')(\text{OR}'')$, $-\text{OP}(\text{O})(\text{OR}')(\text{OR}'')$, $-\text{Si}(\text{R}'\text{R}'')_m(\text{OR}''')_n$ and $-\text{OSi}(\text{R}'\text{R}'')_m(\text{OR}''')_n$ where R' , R'' , R'''

are hydrocarbon radicals optionally unsaturated, having 1-18 carbon atoms, and R' and R'' together, in the case of NR'R'', can also form a cyclic structure, and R' or R'' or both, in the case of -Si(R'R'')_m(OR''')_n and -OSi(R'R'')_m(OR''')_n, can also be hydrogen or halogen, m and n are numbers from 0 to 3, and m+n=3; or X is a R^{IV} hydrocarbyl group having 1-18 carbon atoms containing at least one double bond, and optionally containing one or more heteroatoms selected from the group consisting of halogen, non-ether O, and N, S, P, and Si;

Y is equal to X when X is halogen, -S(R'R'')_m(OR''')_n, or R^{IV} radical, or Y is a hydrogen or an R^V hydrocarbon radical containing 1-18 carbon atoms;

X and Y moreover can be bonded together to form an R^{VI} hydrocarbon radical having 1-18 carbon atoms and optionally containing heteroatoms selected from the group consisting of N, S, P, Si, non-ether O and halogen atoms said R^{VI} being also optionally bonded to the central carbon atom through a double bond.

[0014] Representative example of 1,3-diether containing halogen atoms are:

2-isopropyl-2-trifluoromethyl-1,3-dimethoxypropane;
 2-isopropyl-2-trifluoromethyl-1,3-diethoxypropane;
 2-isopropyl-2-trifluoromethyl-1,3-dibutoxypropane;
 2-isobutyl-2-trifluoromethyl-1,3-dimethoxypropane;
 2-(2-chloro-n-propyl)-2-n-propyl-1,3-dimethoxypropane;
 2-(chloroneopentyl)-2-methyl-1,3-dimethoxypropane;
 2-(4-chloro-3,3-dimethylbutyl)-2-ethyl-1,3-dimethoxypropane;
 2-(p-chloromethylphenyl)-2-isobutyl-1,3-dimethoxypropane;
 2-(p-chloromethylphenyl)-2-isobutyl-1,3-diethoxypropane;
 2-(4-chlorocyclohexyl)-2-isobutyl-1,3-dimethoxypropane;
 2-(4-chlorocyclohexyl)-2-isobutyl-1,3-diethoxypropane;
 2-(4-chlorocyclohexyl)-2-isobutyl-1,3-dibutoxypropane;
 2,2-bis(4-chlorocyclohexyl)-1,3-dimethoxypropane;
 2-(2-chloromethyl-2-propenyl)-2-isobutyl-1,3-dimethoxypropane;
 2-(bromoneopentyl)-2-methyl-1,3-dimethoxypropane;
 2-(bromoneopentyl)-2-ethyl-1,3-dimethoxypropane;
 2-(iodoneopentyl)-2-ethyl-1,3-dimethoxypropane;
 2-(chloromethyl)-2-isobutyl-1,3-dimethoxypropane;
 2-(chloromethyl)-2-isobutyl-1,3-diethoxypropane;
 2-(3-chloro-2-methyl-2-propenyl)-2-propyl-1,3-dimethoxypropane;
 2,2-bis(4-chlorocyclohexylmethyl)-1,3-dimethoxypropane;
 1,1-bis(methoxymethyl)-4-chloro-decahydronaphthalene;
 1,1-bis(methoxymethyl)-6-chloro-tetrahydronaphthalene;
 1,1-bis(methoxymethyl)-2-isopropyl-5-chlorocyclohexane;
 2,2-bis(methoxymethyl)-5-chloro-bicyclo[2.2.1]heptane;
 2-chloro-2-ethyl-1,3-dimethoxypropane;
 2-chloro-2-ethyl-1,3-diethoxypropane;
 2-bromo-2-ethyl-1,3-dimethoxypropane;
 2-chloro-2-n-propyl-1,3-dimethoxypropane;
 2-chloro-2-n-propyl-1,3-diethoxypropane;
 2-chloro-2-n-propyl-1,3-dibutoxypropane;
 2-bromo-2-n-propyl-1,3-dimethoxypropane;
 2-bromo-2-n-propyl-1,3-diethoxypropane;
 2-chloro-2-n-butyl-1,3-dimethoxypropane;
 2-chloro-2-isobutyl-1,3-dimethoxypropane;
 2-chloro-2-isobutyl-1,3-diethoxypropane;
 2-chloro-2-isoamyl-1,3-dimethoxypropane;
 2-chloro-2-isoamyl-1,3-diethoxypropane;
 2-chloro-2-neopentyl-1,3-dimethoxypropane;
 2-chloro-2-cyclohexyl-1,3-dimethoxypropane;
 2-chloro-2-phenyl-1,3-dimethoxypropane;
 2,2-dichloro-1,3-dimethoxypropane;
 2-chloro-2-phenyl-1,3-diethoxypropane;
 2-bromo-2-phenyl-1,3-dimethoxypropane;
 2-chloro-2-trifluoromethyl-1,3-dimethoxypropane;

2-chloro-2-(chloroneopentyl)-1,3-dimethoxypropane;
 2-chloro-2-(4-chlorocyclohexyl)-1,3-dimethoxypropane;
 2-chloro-2-chloromethyl-1,3-dimethoxypropane;
 2-chloro-2-(p-chlorophenyl)-1,3-dimethoxypropane;

[0015] Examples representative of 1,3-diethers containing heteroatoms different from halogens are:

2-trimethylsilyl-1,3-dimethoxypropane;
 2-(2-trimethylsilylethyl)-1,3-dimethoxypropane;
 2-trimethylsilyl-2-ethyl-1,3-dimethoxypropane;
 1-methyl-2-trimethylsilyl-2-ethyl-1,3-dimethoxypropane;
 2-triphenylsilyl-1,3-dimethoxypropane;
 2,2-bis(p-trimethylsilyl-phenyl)-1,3-dimethoxypropane;
 2-(4-[1-silolanyl]-butyl)-2-ethyl-1,3-dimethoxypropane;
 2,2-bis(trimethylsilylmethyl)-1,3-dimethoxypropane;
 2-(4-N,N-diisobutylaminobutyl)-2-ethyl-1,3-dimethoxypropane;
 2-(1-piperidyl)-2-propyl-1,3-dimethoxypropane;
 2-(1-piperidyl)-2-isopropyl-1,3-dimethoxypropane;
 2-(1-piperidyl)-2-n-isobutyl-1,3-dimethoxypropane;
 2-(1-piperidyl)-2-n-propyl-1,3-diethoxypropane;
 2-(1-piperidyl)-2-n-propyl-1,3-dibutoxypropane;
 2-(2,6-dimethyl-1-piperidyl)-2-n-propyl-1,3-dimethoxypropane;
 2-(4-N,N-bis(trimethylsilyl)-aminobutyl)-2-propyl-1,3-dimethoxypropane;
 2-trimethylsilyloxy-2-n-propyl-1,3-dimethoxypropane;
 2-trimethylsilyloxy-2-n-propyl-1,3-diethoxypropane;
 2-trimethylsilyloxy-2-n-propyl-1,3-dibutoxypropane;
 2-trimethylsilyloxy-2-isopropyl-1,3-dimethoxypropane;
 2-trimethylsilyloxy-2-isopropyl-1,3-diethoxypropane;
 2-trimethylsilyloxy-2-isobutyl-1,3-dimethoxypropane;
 2-trimethylsilyloxy-2-isobutyl-1,3-diethoxypropane;
 2-trimethylsilyloxy-2-isoamyl-1,3-dimethoxypropane;
 2-trimethylsilyloxy-2-isoamyl-1,3-diethoxypropane;
 2-benzoyloxy-2-n-propyl-1,3-dimethoxypropane;
 2-benzoyloxy-2-isobutyl-1,3-dimethoxypropane;
 2-trimethylsilyl-2-n-propyl-1,3-dimethoxypropane;
 2-pivaloxy-2-n-propyl-1,3-dimethoxypropane;
 2-t-butylmercapto-2-ethyl-1,3-dimethoxypropane;
 2,2-bis(p-diphenylphosphinophenyl)-1,3-dimethoxypropane;
 2,2-bis(p-pivaloxyphenyl)-1,3-dimethoxypropane;
 2-(3-N,N-diphenylaminopropyl)-2-n-propyl-1,3-dimethoxypropane;
 2-ethyl-2-methoxysulfonyl-1,3-dimethoxypropane;
 2-isopropyl-2-ethylsulfonyl-1,3-dimethoxypropane;
 1,1-bis(methoxymethyl)-1-ethyl-diphenylphosphite;
 1,1-bis(methoxymethyl)-1-ethyl-diphenylphosphate;

[0016] Examples representative of 1-3 ethers containing unsaturations are:

2-(1-ethyl-propylidenyl)-1,3-dimethoxypropane;
 2-(1-ethyl-isobutylidenyl)-1,3-dimethoxypropane;
 2-(1-phenyl-isobutylidenyl)-1,3-dimethoxypropane;
 2-(1-propyl-isoamylidenyl)-1,3-dimethoxypropane;
 2-(1-propyl-butylidenyl)-1,3-dimethoxypropane;
 2-(α -phenyl-benzylidenyl)-1,3-dimethoxypropane;
 2-isoamylidenyl-1,3-dimethoxypropane;
 2-(2-norbornylidenyl)-1,3-dimethoxypropane;
 2-(1-isoamyl-isoamylidenyl)-1,3-dimethoxypropane;
 2-isobutyl-2-(3,3-dimethylallyl)-1,3-dimethoxypropane;
 2-2-bis(3,3-dimethylallyl)-1,3-dimethoxypropane;

2-isobutyl-2-(2-methyl-2-butenyl)-1,3-dimethoxypropane;
 2-isopropyl-2-(5-norbornene-2-yl)-1,3-dimethoxypropane;
 2-isoamyl-2-crotyl-1,3-dimethoxypropane;
 2-cyclopentylidenyl-1,3-dimethoxypropane;
 5 2-isopropyl-2-cinnamyl-1,3-dimethoxypropane;
 2-isobutyl-2-(3-methyl-2-pentenyl)-1,3-dimethoxypropane;
 2,2-bis(3-cyclohexenylmethyl)-1,3-dimethoxypropane;
 2,2-bis(methoxymethyl)-5-norbornene;
 2,3-bis(methoxymethyl)-5-norbornene;
 10 2-isobutyl-2-(1-methylpropenyl)-1,3-dimethoxypropane;
 1-allyl-2,2-dimethyl-1,3-dimethoxypropane;
 2,2-diisobutyl-1-methoxy-3-allyloxypropane;
 2-(1-propyl-isoamylidenyl)-1-methoxy-3-allyloxypropane;
 1-(1-methylpropenyl)-2,2-dimethyl-1,3-dimethoxypropane;
 15 2-(1-methyl-ethylidenyl)-1,3-dimethoxypropane;
 2-(1-isopropyl-isobutylidenyl)-1,3-dimethoxypropane;
 2-(1-t-butyl-isobutylidenyl)-1,3-dimethoxypropane;
 2-(dicyclohexyl-methylidenyl)-1,3-dimethoxypropane;
 2-(1-isopropyl-isohexylidenyl)-1,3-dimethoxypropane;
 20 2-(1-cyclohexyl-isobutylidenyl)-1,3-dimethoxypropane;
 2-(1-ethyl-neopentylidenyl)-1,3-dimethoxypropane;
 2-(1-cyclohexyl-n-propylidenyl)-1,3-dimethoxypropane;
 2-(α -cyclohexyl-benzylidenyl)-1,3-dimethoxypropane;
 2-(1-methyl-neopentylidenyl)-1,3-dimethoxypropane;

[0017] Examples representative of 1,3-diethers containing heteroatoms and unsaturations are:

2-isopropyl-2-(6-chloro-5,5-dimethyl-2-hexenyl)-1,3-dimethoxypropane;
 2-isopropyl-2-(3-chloroallyl)-1,3-dimethoxypropane;
 30 2-isobutyl-2-(5-p-trifluoromethylphenyl)-2-pentenyl-1,3-dimethoxypropane;
 2-methyl-2-(3-chloro-2,2-dimethylpropylidenyl)-1,3-dimethoxypropane;
 2-isopropyl-2-(4-diisobutylamino-2-butenyl)-1,3-dimethoxypropane;
 2-allyl-2-pyridyl-1,3-dimethoxypropane;
 2-isopropyl-2-(4-trimethylsilyl-2-butenyl)-1,3-dimethoxypropane;

[0018] Other examples of usable ethers are:

2,2-diisobutyl-1-methoxy-3-(2-chloroethoxy)propane;
 1-(3-chloro-2-methyl-2-propenyl)-2,2-diisobutyl-1,3-dimethoxypropane;
 40 1-(3-chloropropyl)-2,2-diisobutyl-1,3-dimethoxypropane;
 1-chloro-2,2-diisopropyl-1,3-dimethoxypropane;
 1,3-dichloro-2-isobutyl-1,3-dimethoxypropane;
 1-methyl-2-chloro-2-isopropyl-1,3-dimethoxypropane;
 1-chloro-2-isopropyl-2-isobutyl-1,3-dimethoxypropane;
 45 1-chloro-2,2-diisopropyl-1,3-diethoxypropane;
 2-chloro-2-ethyl-1-methoxy-3-(2-chloroethoxy)propane;
 2-chloro-2-n-propyl-1-methoxy-3-(2-chloroethoxy)propane;
 2-chloro-2-phenyl-1-methoxy-3-(2-chloroethoxy)propane;
 2-chloro-2-ethyl-1,3-bis(2-chloroethoxy)propane;
 50 2-chloro-2-n-propyl-1,3-bis(2-chloroethoxy)propane;
 2-chloro-2-phenyl-1,3-bis(2-chloroethoxy)propane;
 1,3-dichloro-2-isobutyl-1,3-diethoxypropane;
 1,3-dichloro-2-isobutyl-1,3-dibutoxypropane.

[0019] The compounds of the invention are prepared according to methods known in the literature. For example, 2-chloro-2-alkyl-1,3-dialkoxypropanes can be synthesized according to the method described in Vol 65, 3727c of the Chemical Abstracts (1966).

[0020] Ethers containing unsaturations can be synthesized by Wittig reaction starting from the dialkoxyketones and

corresponding phosphorus ylids (obtained by the reaction of triphenylphosphine and alkyl halides).

[0021] 1,3-diethers containing halogens on the hydrocarbon substituents in the 2 position can be synthesized by the reaction of 1,3-diethers, containing unsaturations in the hydrocarbon substituents in the 2 position, and the corresponding hydrogen halides.

[0022] Ethers containing heteroatoms other than halogen can also be prepared according to known methods described in the literature; for example, the 2-alkyl-2-(trialkylsilyloxy)-1,3-dialkoxypromanes can be synthesized by reaction between the 2-hydroxy-2-alkyl-1,3-dialkoxypromanes (obtained by the reaction of a dialkoxycetone and a Grignard) and the corresponding chlorotrialkylsilanes.

[0023] As already indicated the electron-donor compounds of the invention can be used together with Al-alkyl compounds to form, in combination with the catalyst components described in US 4,522,930, highly active and stereospecific catalysts.

[0024] The catalyst components described in US 4,522,930 comprise a titanium compound containing at least one Ti-halogen bond and an electron-donor compound, at least 70 mole% of which is extractable with Al-triethyl under standard extraction conditions. After extraction, the solid has a surface area (B.E.T.) of at least 20 m²/g and generally between 100 and 300 m²/g.

[0025] Electron-donor compounds which can be used in preparing the catalyst components described in US 4,522,930 comprise ethers, ketones, lactones, compounds containing N, P, and/or S atoms, and particular types of esters. Besides the esters of US Patent No. 4,522,930, the class of esters described in European patent No. 0045977 can also be used.

[0026] Particularly suited are phthalic acid esters, such as diisobutyl, dioctyl and diphenylphthalate, benzylbutylphthalate; malonic acid esters, such as diisobutyl and diethylmalonate; alkyl and aryl pivalates, alkyl, cycloalkyl and aryl maleates, alkyl and aryl carbonates, such as diisobutyl carbonate, ethyl phenyl carbonate, and diphenyl carbonate; and succinic acid esters, such as mono and diethyl succinate. Phthalic acid esters are preferred.

[0027] The preparation of catalyst components containing the ethers of the invention is done according to various methods.

[0028] For example, the magnesium halide (used in the anhydrous state containing less than 1% water), the titanium compound, and the ether compound are ground together under conditions where the magnesium halide is activated. The ground product is then treated one or more times with excess TiCl₄ at temperatures from 80° to 135°C, and subsequently washed repeatedly with a hydrocarbon (hexane) until no chloride ions are in the wash.

[0029] According to another method, the anhydrous magnesium halide is preactivated according to known methods, and then reacted with excess TiCl₄ containing the ether compound in solution. In this case the operation also takes place at a temperature from 80° to 135°C. Optionally the TiCl₄ treatment is repeated and the solid washed with hexane or heptane to eliminate the traces of nonreacted TiCl₄.

[0030] According to another method, a MgCl₂-nROH adduct (particularly in the form of spheroidal particles) where n is generally from 1 to 3 and ROH is ethanol, butanol, isobutanol, is reacted with excess TiCl₄ containing the ether compound in solution. The temperature is generally from 80 to 120°C. After reaction the solid is reacted once more with TiCl₄, and then separated and washed with a hydrocarbon until no chloride ions appear in the wash.

[0031] According to yet another method, magnesium alkoxides and alkoxyhalides (the alkoxyhalides can be prepared particularly according to US 4,220,554) are reacted with excess TiCl₄ containing the electron-donor compound of the invention in solution, operating under the same conditions already described.

[0032] According to another method, magnesium halide complexes with titanium alkoxides (the MgCl₂·2Ti(OC₄H₉)₄ complex is a typical example) are reacted, in hydrocarbon solution, with excess TiCl₄ containing the ether compound in solution; the solid product which is separated is reacted again with excess TiCl₄, and then separated and washed with hexane. The reaction with TiCl₄ is done at a temperature from 80 to 120°C.

[0033] According to an alternative embodiment, the MgCl₂ complex with the titanium alkoxide is reacted in hydrocarbon solution with methyl-hydopolysiloxane. The solid product is separated and is reacted at 50°C with silicon tetrachloride containing the ether compound in solution. The resulting solid is then reacted with excess TiCl₄ at 80°-120°C.

[0034] Finally, it is possible to react with the excess TiCl₄ containing the ether compound in solution, porous resins, such as partially crosslinked styrene-divinylbenzene resins in the form of spherical particles, or inorganic porous oxides, such as silica and alumina, impregnated with solutions of Mg compounds or complexes soluble in organic solvents.

[0035] Porous resins which can be used are described in published European 344 755 and corresponding US application Serial No. 359234. The reaction with TiCl₄ is done at 0°-120°C. After separating the excess TiCl₄, the reaction is repeated and the solid is then washed with a hydrocarbon solvent.

[0036] The molar ratio between MgCl₂ and the electron-donor compound used in the above reactions is generally from 2:1 to 12:1.

[0037] The electron-donor compound is generally fixed on the magnesium halide in quantities from 5 to 20 mole%.

[0038] However, in the case of components supported on porous resins and inorganic oxides, the molar ratio between ether and magnesium is different, i.e., generally from 0.1 to 1.

[0039] The Mg/Ti ratio in the catalyst components is generally from 30:1 and 4:1. The ratio is different in components supported on porous resins or inorganic oxides, and is generally from 10:1 to 2:1.

[0040] Titanium compounds which can be used for the preparation of catalyst components are halides and alkoxy-halides. Titanium tetrachloride is the preferred compound. Satisfactory results are obtained also with titanium trihalides, particularly TiCl_3HR , TiCl_3ARA , and with alkoxy halides such as TiCl_3OR where R is a phenyl radical. The preparation methods indicated above can be used also for preparing catalyst components containing electron-donor compounds which are different from the ethers of the invention, such as the ones described in USP 4,522,930, for example.

[0041] The preparations indicated above lead to the formation of magnesium halide in active form. Preparations which lead to the formation of magnesium halide in active form starting from magnesium compounds other than magnesium halides are well known in the literature. Examples of the preparation of catalyst components which lead to the formation of magnesium halides in active form and can be used for the preparation of catalysts according to the invention, are described in the following US patents: US 4,335,015, 4,547,476, 4,647,550, 4,393,182, 4,780,443, 4,771,024.

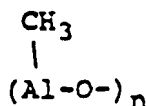
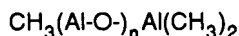
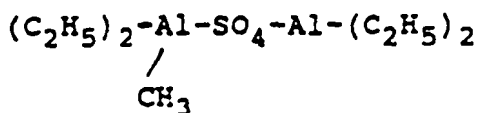
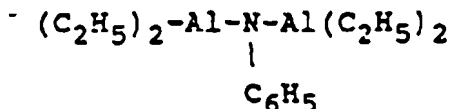
[0042] The active form of magnesium halides in the catalyst components is evidenced by the fact that the X-ray diffraction spectrum of the catalyst component no longer shows the major intensity reflection which appears in the spectrum of nonactivated magnesium halides (having a surface area smaller than $3 \text{ m}^2/\text{g}$), and in its place a halo appears with the maximum intensity shifted with respect to the position of the maximum intensity reflection, or the maximum intensity reflection is less intense and presents a half-peak breadth at least 30% greater than that of the major intensity reflection which appears in the spectrum of the nonactivated Mg halide.

[0043] The most active forms of magnesium halide are those where the X-ray spectrum of the solid catalyst component shows a halo.

[0044] Among the magnesium halides, the magnesium chloride is the preferred compound. In the case of the most active forms of magnesium chloride, the X-ray spectrum of the catalyst component shows a halo instead of the reflection, which in the spectrum of the chloride is situated at the interplanary distance of 2.56 \AA ($1 \text{ \AA} = 0.1 \text{ nm}$).

[0045] In the case of polymerization of $\text{CH}_2=\text{CHR}$ olefins, where R is hydrogen, or an alkyl radical with 1-8 carbon atoms, or aryl, and particularly when the olefin is propylene, the Al-alkyl compounds which can be used are selected from Al-trialkyls such as Al-trimethyl, Al-triethyl, Al-triisobutyl, Al-tri-n-butyl, and linear or cyclic Al-alkyl compounds containing two or more Al atoms linked to each other through O or N atoms, or SO_4 and SO_3 groups.

[0046] Examples of these compounds are:



where n is a number from 1 to 20.

[0047] One can also use $\text{AlR}_2\text{OR}'$ compounds where R' is a $\text{C}_6\text{-C}_{12}$ aryl radical substituted in the 2 and/or 6 position with a $\text{C}_1\text{-C}_6$ alkyl radical linear or branched, and R is an alkyl radical with 1-8 carbon atoms, as well as $\text{Al-R}_2\text{H}$ compounds where R has the above mentioned meaning.

[0048] The Al-alkyl compound is used in such amounts that the Al/Ti ratio is generally from 1 to 1000.

[0049] In the case of polymerisation of propylene and similar alpha-olefins, the trialkyl compounds can be used in mixture with Al-alkyl halides, such as AlEt_2Cl and $\text{Al}_2\text{Et}_3\text{Cl}_3$.

[0050] Polymerization of olefins is carried out according to known methods operating in liquid phase comprising the monomer or monomers, or a solution of same, in an aliphatic or aromatic hydrocarbon solvent, or in gas phase, or even combining polymerization stages in liquid and gas phase.

[0051] (Co)polymerization temperature is generally from 0°C to 150°C ; particularly from 60° to 100°C . The operation takes place under atmospheric pressure or higher. The catalysts can be precontacted with small quantities of olefins (prepolymerization). Prepolymerization improves both the catalyst performance and the morphology of the polymers.

The prepolymerization is carried out maintaining the catalyst in suspension in a hydrocarbon solvent (hexane, heptane etc.) and it is polymerised at a temperature between room temperature and 60°C , producing quantities of polymer generally from 0.5 and 3 times the weight of the catalyst. It can also be done in liquid propylene, under the temperature conditions indicated above, thus producing quantities of polymer which can reach 100 g per g of catalyst component.

[0052] The ratio between Al-alkyl and electron-donor compound is generally from 5:1 to 100:1.

[0053] The following examples are given in order to illustrate, but not limit the invention.

Example 1

[0054] 1000 ml n-heptane, 5 mmoles $\text{Al}(\text{C}_2\text{H}_5)_3$, 30 mg catalyst component, and 1 mmole 2-(2-chloro-n-propyl)-2-n-propyl-1,3-dimethoxypropane are introduced in a stainless steel 2000 ml autoclave equipped with anchor stirrer under propylene current at 25°C .

[0055] The autoclave is closed, and after the pressure is brought to 1 atm, a hydrogen overpressure equal to 0.2 atm is introduced. The content is then heated to 70°C and the total pressure is brought to 7 atm with propylene.

[0056] Polymerization is carried out for 2 hours while the monomer is fed continuously. The polymer thus obtained is separated by filtration. The polymer which remained in the filtrate is precipitated with methanol, dried in vacuum and considered in the determination of the total n-heptane extraction residue. A polymer yield equal to 8000 g of PP/g of catalyst component and having a 92 isotactic index are obtained.

[0057] The catalyst component which was used was prepared with the following methods.

[0058] 225 ml of TiCl_4 are introduced at 0°C in a 500 ml reactor equipped with filtering septum. Over 15 minutes are added, under agitation, 10.1 g (54 mmoles) of microspheroidal adduct $\text{MgCl}_2 \cdot 2.1\text{C}_2\text{H}_5\text{OH}$ obtained with the method described in example 1 of US 4,469,648.

[0059] Once the addition is completed, the temperature is brought to 40°C , and 9 mmoles of diisobutylphthalate are introduced. The temperature is then brought to 100°C in 1 hour. The reaction is allowed to proceed for 2 hours, after which the TiCl_4 is removed by filtration. An additional 200 ml of TiCl_4 are introduced, and the contents are allowed to react at 120°C for 1 hour, and then filtered and washed at 60°C with n-heptane until no chloride ions appear in the filtrate.

Example 2

[0060] Operating under the conditions of example 1, but using 1 mmole of 2-(1-methyl-neopentylidene)-1,3-dimethoxypropane instead of 2-(2-chloro-n-propyl)-2-n-propyl-1,3-dimethoxypropane a polymer having an isotactic index of 95 with a yield equal to 10,000 g PP/g catalyst component is obtained.

Example 3

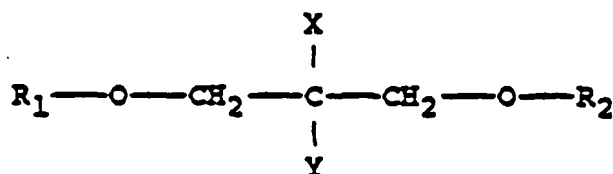
[0061] Operating under the conditions of example 1, but using 1 mmole of 2-n-propyl-2-trimethylsilyloxy-1,3-dimethoxypropane instead of 2-(2-chloro-n-propyl)-2-n-propyl-1,3-dimethoxypropane, a polymer having an isotactic index of 93.9 with a yield equal to 4300 g of PP/g of catalyst component is obtained.

Claims

1. A catalyst for the polymerization of olefins comprising the reaction product of:

a) an Al-alkyl compound,

b) an ether compound containing two ether groups and at least one heteroatom or at least one double bond, or both at least one heteroatom and at least one double bond, said ether compound having formula



where

R_1 and R_2 are the same or different and are hydrocarbon radicals with 1-6 carbon atoms, optionally unsaturated and/or containing halogen atoms;

X is a hydrocarbon radical having 1-18 carbon atoms, containing at least one heteroatom which is not directly bonded to the central carbon atom (in the 2 position) of the 1,3-diether molecules, wherein the heteroatom is selected from the group consisting of N, S, P, Si, non-ether O and halogen atoms, or

X is a halogen atom or a heteroatom-containing group wherein one heteroatom is bonded directly to the central carbon atom of the 1,3-diether of the above formula and which is selected from the group consisting of $-\text{NR}'\text{R}''$, $-\text{SO}_2\text{R}'$, $-\text{SOR}'$, $-\text{OP}(\text{OR}')(\text{OR}'')$, $-\text{OP}(\text{O})(\text{OR}')(\text{OR}'')$, $-\text{Si}(\text{R}'\text{R}'')_m(\text{OR}''')_n$ and $-\text{OSi}(\text{R}'\text{R}'')_m(\text{OR}''')_n$

where R' , R'' , R''' are hydrocarbon radicals optionally unsaturated, having 1-18 carbon atoms, and R' and R'' together, in the case of $\text{NR}'\text{R}''$, can also form a cyclic structure, and R' or R'' or both, in the case of $-\text{Si}(\text{R}'\text{R}'')_m(\text{OR}''')_n$ and $-\text{OSi}(\text{R}'\text{R}'')_m(\text{OR}''')_n$, can also be hydrogen or halogen, m and n are numbers from 0 to 3, and $m+n=3$; or X is a R^{IV} hydrocarbonyl group having 1-18 carbon atoms containing at least one double bond, and optionally containing one or more heteroatoms selected from the group consisting of N, S, P, Si, non-ether O and halogen atoms;

Y is equal to X when X is halogen, $-\text{Si}(\text{R}'\text{R}'')_m(\text{OR}''')_n$, or R^{IV} radical, or Y is a hydrogen or an R^{V} hydrocarbon radical containing 1-18 carbon atoms;

X and Y moreover can be bonded together to form an R^{VI} hydrocarbon radical having 1-18 carbon atoms and optionally containing heteroatoms selected from the group consisting of halogen, non-ether O, and N, S, P and Si, said R^{VI} being also optionally bonded to the central carbon atom through a double bond, 2-(p-chlorophenyl)-1,3-dimethoxypropane and 2-(p-fluorophenyl)-1,3-dimethoxypropane being excluded,

and

c) a solid catalyst component comprising a magnesium dihalide in active form having supported thereon a titanium halide or alkoxyhalide and an electron-donor compound, at least 70% in moles of which can be extracted from the solid with Al-triethyl, and wherein the solid catalyst component, after extraction, has a surface area greater than 20 m^2/g .

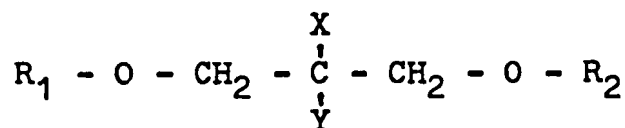
2. The catalyst of claim 1 wherein the Al-alkyl compound is an Al-triethyl, and the electron-donor compound present in component c) is a phthalic acid ester.

Patentansprüche

1. Katalysator für die Polymerisation von Olefinen, umfassend das Reaktionsprodukt von

a) einer Al-alkylverbindung,

b) einer Etherverbindung, enthaltend zwei Ethergruppen und zumindest ein Heteroatom oder zumindest eine Doppelbindung oder sowohl zumindest ein Heteroatom als auch zumindest eine Doppelbindung, wobei dieser Etherverbindung die Formel



besitzt, worin

R_1 und R_2 gleich oder voneinander verschieden sind und Kohlenwasserstoffreste mit 1 bis 6 Kohlenstoffatomen, gegebenenfalls ungesättigt und/oder Halogenatome enthaltend, bedeuten;

X einen Kohlenwasserstoffrest mit 1 bis 18 Kohlenstoffatomen, enthaltend zumindest ein Heteroatom, das nicht direkt gebunden ist an das zentrale Kohlenstoffatom (in 2-Stellung) der 1,3-Diethermoleküle, bedeutet, worin das Heteroatom ausgewählt ist unter N-, S-, P-, Si-, Nicht-Ether O- und Halogenatomen, oder

X ein Halogenatom oder eine heteroatomhaltige Gruppe ist, worin ein Heteroatom direkt an das zentrale Kohlenstoffatom des 1,3-Diethers der vorstehenden Formel gebunden ist und welche ausgewählt ist aus $-NR'R''$, $-SO_2R'$, $-SOR'$, $-OP(OR')(OR'')$, $-OP(O)(OR')(OR'')$, $-Si(R'R'')(OR'')_m$ und $-OSi(R'R'')(OR'')_n$, worin R' , R'' , R''' Kohlenwasserstoffreste, gegebenenfalls ungesättigt, mit 1 bis 18 Kohlenstoffatomen bedeuten und R' und R'' gemeinsam im Fall von $NR'R''$ auch eine cyclische Struktur bilden können, und R' oder R'' oder beide im Fall von $-Si(R'R'')(OR'')_m$ und $-OSi(R'R'')(OR'')_n$ auch Wasserstoff oder Halogen sein können, m und n ganze Zahlen von 0 bis 5 sind und $m+n=3$; oder

X eine Hydrocarbylgruppe R^{IV} mit 1 bis 18 Kohlenstoffatomen bedeutet, welche zumindest eine Doppelbindung enthält und gegebenenfalls ein oder mehrere Heteroatome, ausgewählt unter N-, S-, P-, Si-, Nicht-Ether O- und Halogenatomen, umfaßt;

Y die Bedeutung von X hat, wenn X Halogen, $-Si(R'R'')(OR'')_m$ oder einen Rest R^{IV} bedeutet oder Y Wasserstoff oder einen Kohlenwasserstoffrest R^V mit 1 bis 18 Kohlenstoffatomen wiedergibt;

X und Y darüber hinaus miteinander verbunden sein können unter Bildung eines Kohlenwasserstoffrestes R^{VI} mit 1 bis 18 Kohlenstoffatomen, der gegebenenfalls Heteroatome, ausgewählt unter Halogen, Nicht-Ether O und N, S, P und Si, enthält, wobei dieses R^{VI} gegebenenfalls auch an das zentrale Kohlenstoffatom über eine Doppelbindung gebunden ist, wobei 2-(p-Chlorphenyl)-1,3-dimethoxypropan und 2-(p-Fluorphenyl)-1,3-dimethoxypropan ausgenommen sind; und

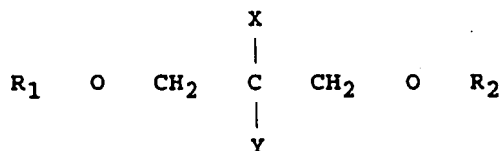
c) einer festen Katalysatorkomponente, umfassend ein Magnesiumdihalogenid in aktiver Form, das hierauf aufgebracht ein Titanhalogenid oder -alkoxyhalogenid und eine Elektronendonoreverbindung aufweist, von der zumindest 70 Mol-% aus dem Feststoff mit Al-triethyl extrahiert werden können, und worin die feste Katalysatorkomponente nach der Extraktion eine spezifische Oberfläche von größer als 20 m²/g besitzt.

2. Katalysator gemäß Anspruch 1, worin die Al-alkyl-verbindung ein Al-triethyl ist und die in Komponente c) anwesende Elektronendonoreverbindung ein Phthalsäureester ist.

Revendications

1. Un catalyseur pour la polymérisation d'oléfines comprenant le produit de variation de :

- a) un dérivé alkyl-Al,
b) un dérivé éther contenant deux groupes éther et au moins un hétéroatome ou au moins une double liaison ou à la fois au moins un hétéroatome et au moins une double liaison, ledit composé éther répondant à la formule



dans laquelle R_1 et R_2 sont identiques ou différents et sont des radicaux hydrocarbonés comportant de 1 à 6 atomes de carbone, éventuellement insaturés et/ou contenant des atomes d'halogène ;

X est un radical hydrocarboné ayant 1 à 18 atomes de carbone, contenant au moins un hétéroatome qui n'est pas directement lié à l'atome de carbone central (en position 2) de la molécule de 1,3-diéther, où l'hétéroatome est choisi parmi le groupe consistant en N, S, P, Si, O non-éther et atome d'halogène, ou bien X est un atome d'halogène ou un groupe contenant un hétéroatome dans lequel un hétéroatome est fixé directement à l'atome de carbone central du 1,3-diéther de la formule mentionnée ci-dessus et qui

est choisi dans le groupe consistant en $-NR'R''$, $-SO_2R'$, $-SOR'$, $-OP(OR')(OR'')$, $-OP(O)(OR')(OR'')$, $-Si(R'R'')(OR'')_n$ et $OSi(R'R'')(OR'')_n$ où R' , R'' , R''' sont des radicaux hydrocarbonés éventuellement insaturés, comportant 1 à 18 atomes de carbone et R' et R'' , ensemble, dans le cas de $NR'R''$, peuvent également être former une structure cyclique, et R' ou R'' ou les deux, dans le cas de $-Si(R'R'')(OR'')_n$ et $-OSi(R'R'')(OR'')_n$, peuvent également être un hydrogène ou un halogène, m et n sont des nombres de 0 à 3 et $m+n=3$; ou

bien X est un groupe hydrocarbyle R^{IV} ayant 1 à 18 atomes de carbone contenant au moins une double liaison, et le cas échéant, contenant un ou plusieurs hétéroatomes choisis dans le groupes consistant N, S, P et Si, O non éther et atomes d'halogène;

Y est égal à X lorsque X est un halogène, $-Si(R'R'')(OR'')_n$, ou un radical R^{IV} , ou bien Y est un hydrogène ou un radical hydrocarboné ou un radical hydrocarboné R^V comportant de 1 à 18 atomes de carbone; X et Y en outre, peuvent être liés ensemble pour former un radical hydrocarboné R^{VI} ayant 1 à 18 atomes de carbone et contenant éventuellement des hétéroatomes choisis dans le groupe consistant en halogène, O non-éther et N, S, P, Si, ledit R^{VI} étant également éventuellement lié à l'atome de carbone central par l'intermédiaire d'une double liaison, le 2-(p-chlorophényl)-1,3-diméthoxypropane et le 2-(p-fluorophényl)-1,3-diméthoxypropane étant exclus et

c) un composant de catalyseur solide comprenant un dihalogénure de magnésium sous forme active qui supporte un halogénure ou un alcoxyhalogénure de titane et un composé donneur d'électron, dont 70 % molaires peuvent être extraits du solide par le triéthyl-Al et où le composant de catalyseur solide après extraction a une surface spécifique supérieure à 20 m²/g.

2. Le catalyseur selon la revendication 1 dans lequel le composé alkyl-Al est un triéthyl-Al et le composé donneur d'électron présent dans le composant c) est un ester d'un acide phtalique.